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Vibrational spectra of cholesterol derivative and its assignments

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Abstract : The FT-laser Raman spectrum of Tosyl Cholesterol molecule was recorded using Nd-YAG laser operating at 1064 nm as a source of excitation in the region of 50–3500 cm^{-1}. The FTIR spectra of above molecule have also been recorded in the solid phase as well as in the liquid phase in the regions of 400–4000 cm^{-1}. The molecule has been assumed to belong to Cs- point group. Symmetric and asymmetric vibrations have been explained to *a'* and *a"* respectively. These molecular vibrations have been correlated with the vibrations observed in the FTIR spectrum of the said molecule.

Keywords : Vibrational spectra, Tosyl Cholesterol, assignments.

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1. Introduction

Steroids include sterols, bile acids, sex hormones, vitamin D, corticoids, sapogenins and alkaloids. These compounds have been found to be of highly biological activity. These are important compounds to prepare the drugs for several ailments in the body. The steroids and their derivatives have been the subject of spectroscopic studies in infrared region and the earlier works on the infrared absorption spectra of steroids include those of Jones and Herling [1], Jones and Standrofy [2]. An atlas containing infrared spectra of large number of steroids has been studied by Dobrin, Katzenellenbogen and Jones [3,4]. Recently, Agarwal and Verma [5] have reported the infrared spectra of C6-Spiro steroidal tetrazene and its chloro, bromo, iodo, and acetate derivatives. Infrared spectra of cholestane 3-one and cholestane-7-one have been investigated by Jones [6]. The Raman spectra of steroids were not reported in the literature earlier. Therefore, it is desirable to record the laser Raman spectra of steroids to give the detailed vibrational analysis. The present paper deals with FT-laser Raman spectra of steroid, namely, Tosyl Cholesterol along with the FTIR spectrum. The observed vibrational bands have been analyzed in terms of fundamentals, combinations and difference vibrational frequencies and probable modes have been assigned.

2. Experimental details

The above steroid has been prepared in Steroidal Research Laboratory, Department of Chemistry, Aligarh Muslim University, Aligarh. The molecular structural formulae of Tosyl Cholesterol has been shown in the Figure 1. It was in solid form at room temperature and was used as such for recording the FT-infrared and the FT-laser Raman spectra. The FTIR spectra of the compound was recorded in solid phase using KBr pellets technique as well as in the liquid phase using methanol as a solvent in the regions of 400–4000 cm^{-1} on Perkin-Elmer FTIR spectrophotometer equipped with computer datamate. The resolution of the FTIR spectrophtometer was 4.0 cm^{-1}. These were recorded in the Chemistry Department of

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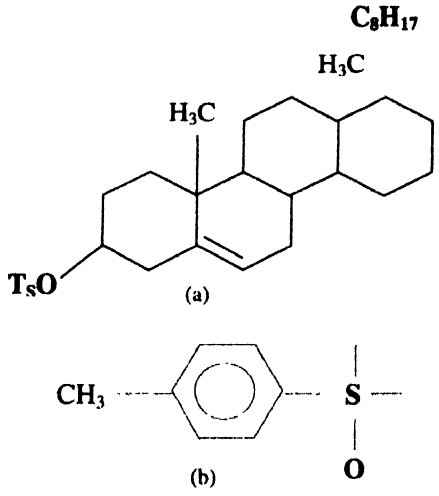

Figure 1. (a) The molecular structure formula of Tosyl Cholesterol and (b) structure of Ts (Tosyl) group.

Delhi University, Delhi. The traces of these spectra have been shown in Figures 2 and 3. The FT-Raman spectrum of the compound was also recorded using Bruker IFS FT-Raman spectrometer at I I T Chennai. It was obtained in the range of 50–3500 cm^{-1} using Nd-YAG laser at a wavelength of 1064 nm 200 mW power and a germanium diode detector. This spectrum is presented in Figure 4.

3. Results and discussion

FT-laser Raman and FTIR spectra of steroid are complex due to fact that its structure is not a simple and uniform one. Vibrational spectra of complex polyatomic molecules play an important role to recognize the various vibrations. In this paper, we have studied the complete vibrational analysis of the steroid, namely, Tosyl Cholesterol through FT-laser Raman and FTIR spectra. It is the Tosyl derivative of 3β-hydroxy Cholest-5-ene (Cholesterol). H in the place of 3β-position has been replaced by Tosyl group (Ts). Ts group *i.e.* p-toluene sulfonyl group contains an aromatic ring. If we assume as an approximation that each of the substituent groups as a single point mass lying in the plane of the molecule, the molecule may belong to *Cs*-point group, having only one element of symmetry *i.e.* molecular plane containing all atoms. This molecule has only two types of vibrations *i.e.* planar (*a'*)

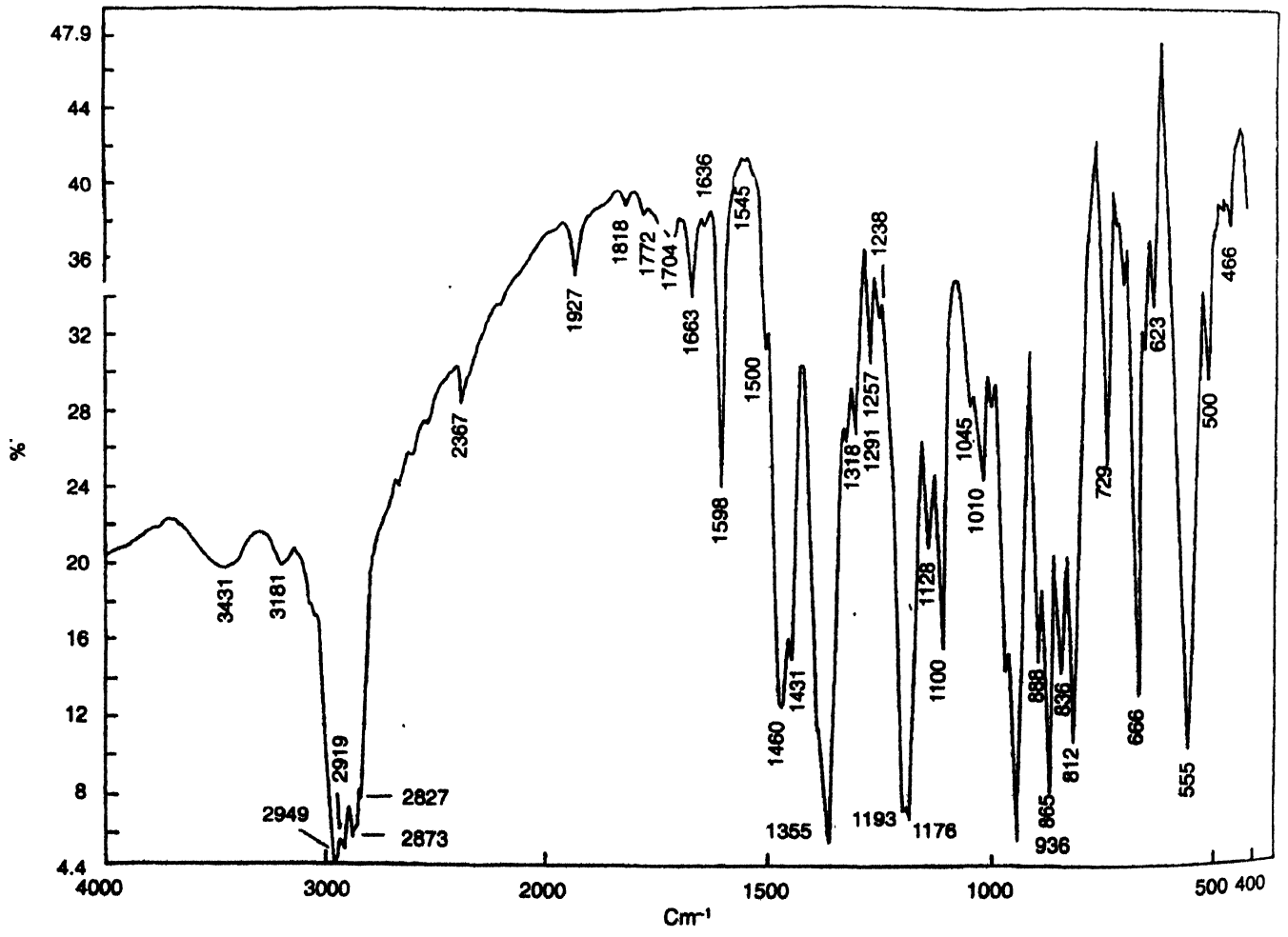

Figure 2. FTIR spectrum of Tosyl Cholesterol (solid phase).

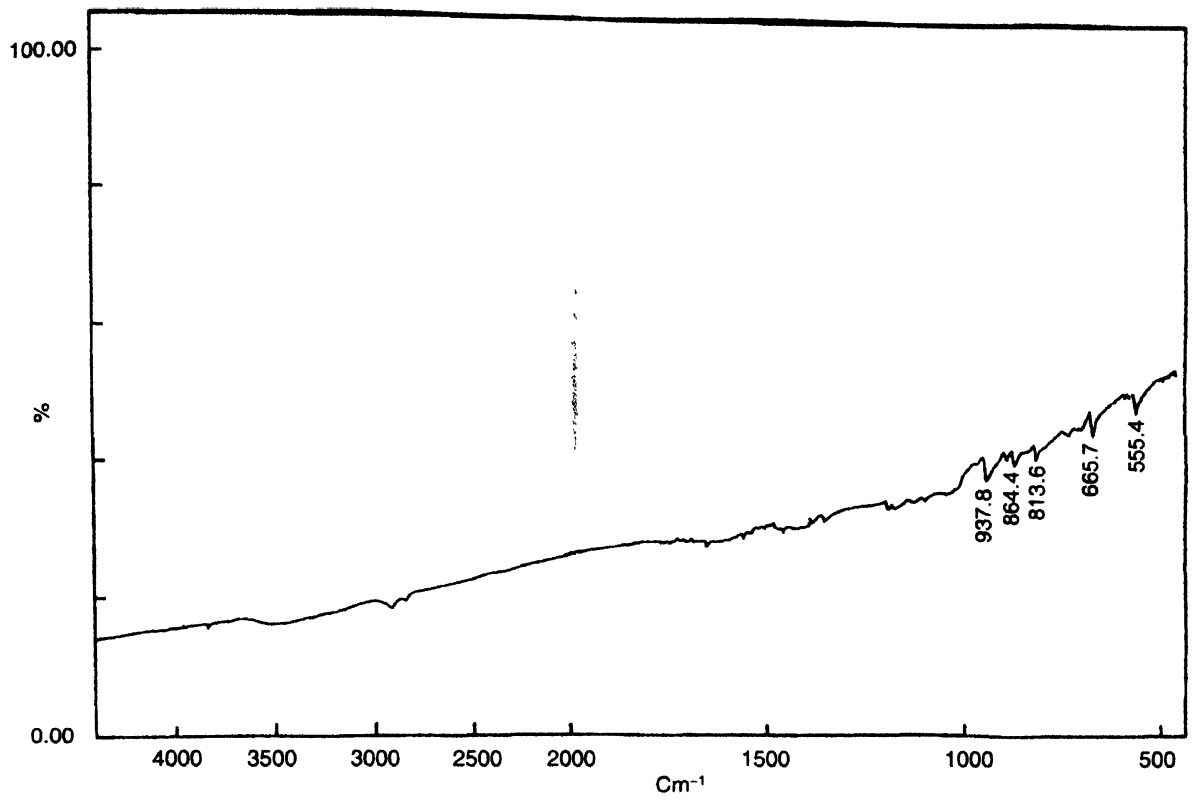

Figure 3. FTIR spectrum of Tosyl Cholesterol in methanol (liquid phase).

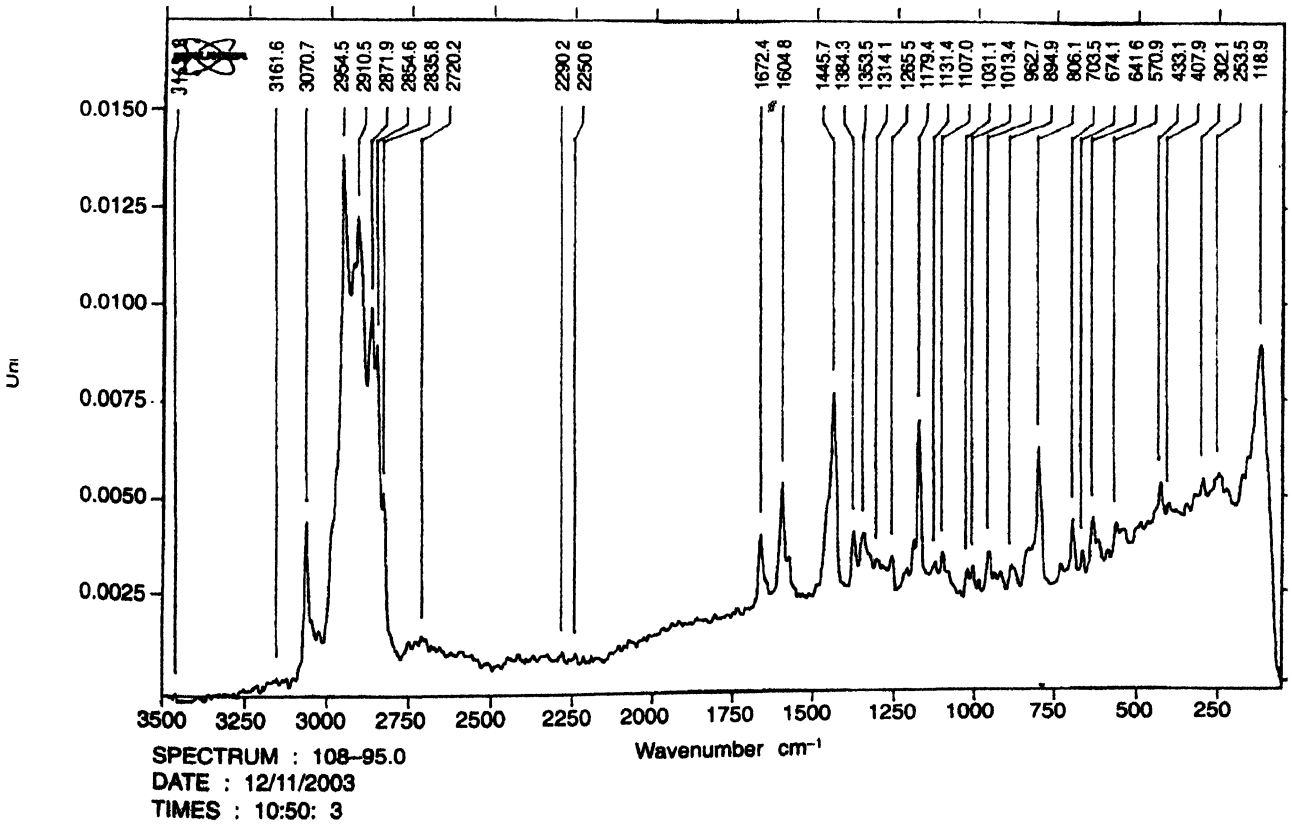

Figure 4. FT-laser Raman spectrum of Tosyl Cholesterol.

and non-planar (a'') and will be active in both infrared and Raman. The observed vibrational frequencies with relative intensities and probable assignments are presented in the Tables 1 and 2. From the FTIR spectra of the compound in solid phase and in the liquid phase *i.e.* in the solution of methanol, it has been observed that vibrational spectrum of the compound is affected by the environmental factors; as a result, the changes in shape, frequency and intensity of bands are observed. The frequency shifts observed in these spectra have been given in Table 3. The measurements of these spectral changes due to solvent, may throw some light on the intermolecular forces. Therefore, the structural property of the methanol molecule gives rise to the break of the internal hydrogen bonding of solid and stabilize the open structure by means of the solute-solvent interactions.

3.1. C–H stretching ring vibrations :

Since the overlap of absorption bands is appreciable in this region (3000–2850 cm^{-1}), little information of the structure can be obtained from the C–H stretching vibrations of methyl and methylene groups in steroids. The C–H bands attached to the unsaturated groups are, however, readily distinguished by their high stretching frequencies (>3000 cm^{-1}). In the present investigation, the bands observed in FTIR spectrum at 3034 and 3057 cm^{-1} have been assigned to C–H stretching vibrations. In the FT-Raman spectrum, the above band has appeared at 3070.7 cm^{-1}. The above assignments are in good agreement with the earlier reports [5,7–9].

3.2. C–H in-plane deformation and ring breathing modes :

A number of characteristic absorption bands in the region 1100–1300 cm^{-1} are due to C–H in-plane deformation. The position and number of C–H in-plane deformation modes depend on the orientation and number of the isolated-ring hydrogen atoms. In this paper, the bands observed at 1128, 1178, 1193, 1238, 1257 and 1291 cm^{-1} in FTIR spectrum have been assigned to C–H in-plane bending vibrations. Their counter part bands have been observed at 1131.4, 1179.4 and 1265.5 cm^{-1} in the FT-laser Raman spectrum. These results agree very well with earlier work [2,10,11]. Ring breathing vibration modes generally occur around 1000 cm^{-1}. In the present investigation, this vibration has appeared at 1010 cm^{-1} in FTIR and at 1013.4 cm^{-1} in FT-Raman spectrum of Tosyl Cholesterol. This band was assigned at 1010 cm^{-1} in Ref. [12].

Table 1. Observed vibrational frequencies in FTIR spectrum of Tosyl Cholesterol and their probable assignments.

IR frequency in cm^{-1}	Intensity	Symmetry species	Proposed vibrational assignements
466	2.0	a''	C–C o.p.b
488	1.0	a''	C–C o.p.b
500	4.2	a''	C–S o.p.b
555	9.5	a'	C–C i.p.b
623	3.2	a'	C–C i.p.b
659	1.0	a''	C–H o.p.b
666	8.5	a''	C–H o.p.b
704	2.0	a''	C–H o.p.b
715	1.0	a'	C–S stretch.
729	6.0	a''	CHs rocking
812	7.5	a''	C–H o.p.b
836	5.0	a''	C–H o.p.b
865	6.5	a'	S–O stretch.
888	3.0	a'	S–O sretch.
939	10.0	a'	S–O stretch.
988	1.0	a'	C–C stretch.
1010	2.5	a'	Ring breathing vib.
1045	1.0	a''	$C–CH_3$ rocking
1100	5.0	a''	$C–CH_3$ rocking
1128	3.0	a'	C–H i.p.b
1176	9.0	a'	C–H i.p.b
1193	1.0	a'	C–H i.p.b
1238	1.0	a'	C–H i.p.b
1257	3.0	a'	C–H i.p.b
1291	2.0	a'	C–H i.p.b
1318	1.0	a'	C–O stretch.
1355	10.0	a''	Angular CH_3 group b/w two six membered rings (C-
1431	2.0	a''	$C–CH_3$ asy. def.
1460	4.0	a''	CH_2 scissoring
1500	2.0	a'	C–C stretch.
1545	1.0	a'	C–C stretch.
1598	6.0	a'	C–C stretch.
1636	1.0	A'	(1010 + 623)
1663	3.0	A'	(1010 + 659)
1704	2.0	A'	(1010 + 704)
1772	1.0	A'	(1128 + 666)
1818	1.0	A''	(1318 + 500)
1927	2.5	A''	(1460 + 466)
2184	1.0	A'	(1176 + 1010)
2376	2.5	A''	(1355 + 1010)
2528	1.0	A'	(2 × 1257)
2597	1.0	A''	(1238 + 1355)
2620	1.0	A''	(1431 + 1193)
2827	1.5	a'	CH_2 sym. stretch.

Table 1. *(Cont'd)*

IR frequency in cm^{-1}	Intensity	Symmetry species	Proposed vibrational assignements
2873	1.5	*a'*	CH_3 in-phase stretch.
2919	1.5	*a"*	CH_2 asy. stretch.
2949	1.5	*a"*	CH_3 out-of-phase stretch
3034	1.0	*a'*	C–H stretch.
3057	1.0	*a'*	C–H stretch.
3181	3.0	*A'*	(2 × 1589)
3431	3.0	*A'*	(2873 + 555)

Table 2. Observed vibrational frequencies in FT-laser Raman spectrum of Tosyl Cholesterol and their probable assignments.

frequency in cm^{-1}	Symmetry species	Assignement
118.9		CH_3 torsional
253.5		(1265–1013)
302.1		(1314–1013)
407.9	*a'*	C–C o.p.b
433.1	*a'*	C–C o.p.b
570 9	*a'*	C–C i.p.b
641.1	*a"*	C–H o.p.b
674.1	*a"*	C–H o.p.b
703.5	*a"*	C–H o.p.b.
806.1	*a"*	C–H o.p.b
894.9	*a'*	S–O stretch.
962.7	*a'*	S–O stretch.
1013.4	*a'*	Ring breathing vib.
1031.1	*a"*	C–CH_3 rocking.
1107.0	*a"*	C–CH_3 rocking
1131 4	*a'*	C–H i.p.b.
1179.4	*a'*	C–H i.p.b.
1265.5	*a'*	C–H i.p.b
1314.1	*a'*	C–O stretch.
1353.5	*a"*	Angular methyl group b/w two six membered rings (C-10)
1384.3	*a"*	Angular methyl group b/w a six and a five membered rings (C-18)
1445.7	*a"*	C–CH_3 asy. def.
1604.8	*a'*	C–C stretch.
1672.4	*A'*	(1031 + 641)
2250.6	*A"*	(1604 + 641)
2290.2	*A"*	(1265 + 1031).
2720.2	*A"*	(1604 + 1107)
2835.8	*a'*	CH_2 sym. stretch.
2854.6	*a"*	CH_2 asy. stretch.
2871.9	*a'*	CH_3 in phase stretch.
2910.5	*a"*	CH_2 asy. stretch.
2954.5	*a"*	CH_3 out-of-phase stretch.
3070.7	*a'*	C–H stretch.
3161.6	*A"*	(2 × 1265 + 641)
3469.8	*A"*	(3070 + 407))

Table 3. Observed frequency shifts in Tosyl Cholesterol in methanol.

FTIR freqency in KBr Pellet (cm^{-1})	FTIR frequency in solvent	Shifts in frequency	Assignments
2919.5	2925.0	5.5	CH_2 asy. stretch.
2873.6	2850.0	23.6	CH_3 in phase stretch.
988.0	975.5	12.5	C–C stretch.
939.92	937.8	2.12	S–O stretch
865.94	864.4	1.54	S–O stretch.
812.62	813.6	0.98	C–H o.p.b
729.67	738.0	8.33	CH_2 rocking
704.55	700.0	4.55	C–H o.p.b
666.87	665.7	1.10	C–H o.p.b
555.08	555.4	0.32	C–C i.p.b.

asy. stretch.– asymmetric stretching, o.p.b.– Out-of-plane bending, i.p.b.– In-plane-bending, asy. def.– asymmetric deformation, sym. stretch.– symmetric stretching.

3.3. C–H out-of-plane bending vibrations :

Bands appearing in the region (700–900 cm^{-1}) have been attributed to C–H out-of-plane bending vibrations and positions of these bands depend on the number of free hydrogen atoms adjacent to one another. In the present paper, these bands have been found at 659, 666, 704, 812 and 836 cm^{-1} in FTIR spectrum. The above bands in FT-laser Raman spectrum were obtained at 641.6, 674.1 and 806.1 cm^{-1}. These vibrations are in favourable agreement with the values given in the literature [12–15].

3.4. C–S stretching vibrations :

The C–S stretching frequencies generally appear as a band of weak or moderate intensity in the range of 720–570 cm^{-1}. Bellamy [16] has suggested that C–S stretching vibration normally appears in the infrared as a weak absorption in the range of 700–600 cm^{-1} and C–S out-of-plane bending vibration at nearly 500 cm^{-1}. In the present study, the band observed at 715 cm^{-1} has been assigned to C–S stretching vibration in the FTIR spectrum. This frequency was identified at 700 cm^{-1} in (C6-SPT) by Agarwal and Verma [5]. A band observed at 500 cm^{-1} has been assigned as C–S out-of-plane bending vibration in the FTIR spectrum of the compound. A C–S stretching vibration has been assigned at 695 cm^{-1} by [17]. The above assignments also agree with those of Refs. [18–20]. Ruifeng *et al* [18] and Stuart [19] have obtained C–S stretching vibrational frequencies at 735 and at 732 cm^{-1}, respectively.

3.5. S–O stretching vibrations :

Rao [21] and Bellamy [16] have suggested that S–O stretching vibrations occur in the region of 890–950 cm^{-1}.

The S–O stretching frequency has been observed as a strong band around 900 cm^{-1} by [22] and around 860 cm^{-1} by [23]. In the light of the above discussion, here, the bands observed at 865, 888 and 939 cm^{-1}, have been assigned to S–O stretching vibrations in FTIR spectrum and in FT-laser Raman spectrum, these are at 894.9 and 962.7 cm^{-1} of the compound.

3.6. Angular methyl group vibrations :

Rao [21] has suggested that the vibrations of angular methyl group in between two six-membered rings (C-10) are in the region of 1374–1392 cm^{-1} and are in between a five and a six-membered ring (C-18) in the region of 1372–1383 cm^{-1}. The above vibrations have been assigned at 1385 cm^{-1} and at 1370 cm^{-1} in (C6-SPT) our earlier work [5]. In the light of the above results, in the present investigation, the vibrations obtained at 1353.5 and at 1355 cm^{-1} in FT-laser Raman and in FTIR spectra respectively, are assigned to the angular methyl group vibrations in between two six-membered rings (C–10). The vibration appeared at 1387.3 in FT-laser Raman spectrum of the same is assigned to angular methyl group vibration in between a five and a six-membered ring (C-18).

The rocking vibrations of CH_3 group interact with other modes as a result of which the rocking mode frequency is not consistent. Several workers [24,25] have assigned these vibrations at about 1170 ± 40 cm^{-1}. Rangacharyulu and Premaswarup [26] have assigned out-of-plane rocking mode of CH_3 group at 1050 cm^{-1} in 2-bromo-5-nitrotoluene, at 1080 cm^{-1} in 2-bromo-4-nitrotoluene, at 1080 cm^{-1} in 4-chloro-3-nitrotoluene. In the present investigation, this vibration has been assigned at 1045 cm^{-1} in FTIR spectrum. Their counter parts has been assigned at 1031 cm^{-1} in FT-laser Raman spectrum. Ahmed and Verma [27] have reported this vibration at 1135 cm^{-1} in 3,4,5-trimethoxybenzaldehyde. Agarwal and Verma [5] have assigned this vibration at 1060 cm^{-1} in the infrared spectra of C6-Spiro steroidal tetrazenes.

Shukla *et al* [28] have observed a very weak Raman line at 184 cm^{-1} in 2,3-dimethylaniline. In the present study, we have observed a Raman line at 118 cm^{-1} in FT-laser Raman spectrum which we have assigned tentatively to this mode. The asymmetric deformations of the substituent methyl groups are to be expected in the region of 1410–1470 cm^{-1}. Shukla *et al* [28] have shown the Raman spectrum in which the frequencies 1462, 1450, 1443, 1438 cm^{-1} were assigned to C–CH_3 asymmetric deformations. The above band has been found at 1445 cm^{-1} in FT-laser Raman spectrum. Some of these frequen-cies are also observed in the infrared spectra. In the present paper, the two bands are seen at 1431 and 1469 cm^{-1} in FTIR spectrum.

In the spectra of 2,3-dimethylaniline, four asymmetric CH_3 stretching are expected [29] in the range of 2925–2900 cm^{-1}. Shukla *et al* [28] have found the above vibrations at 2941, 2967 and at 2978 cm^{-1}. Agarwal and Verma [5] have shown the CH_3 asymmetric stretching vibrational frequencies at 2960, 2970, 2960 and at 2960 cm^{-1} in chloro, bromo, iodo and acetate derivatives of C6-Spiro-steroidal tetrazenes respectively. In the present paper, the C–CH_3 out-of-phase stretching have been assigned at 2949 in FTIR spectrum. In FT-laser Raman spectrum, the above symmetric and asymmetric CH_3 vibrations have been explained at 2871.9 and 2954.5 cm^{-1}. Verma *et al* [5] have found the CH_3 in-phase stretching at 2870, 2860, 2875 and 2870 cm^{-1} in infrared spectra of chloro, bromo, iodo and acetate C6-Spiro-steroidal tetrazenes respectively. In the present investigation, the CH_3 in-phase stretching vibrational frequency has been assigned at 2873 cm^{-1} in the undertaken compound. CH_3 asymmetric stretching and symmetric stretching vibrational frequencies have been assigned at 2965 and 2853 cm^{-1} in IR spectrum of isomeric methoxybenzaldehyde by Singh *et al* [30]. The vibrational studies of 5,6-dihydro-5-methyl uracil by Krishna Kumar and Ramaswamy [31] have identified the CH_3 symmetric and asymmetric bands at 2933 and 2980 cm^{-1} respectively.

3.7. CH_2 vibrations :

Krishna Kumar and Ramaswamy [31] have identified the CH_2 symmetric and asymmetric bands at 2839 and 2890 cm^{-1} respectively. In view of the above finding, in the present study, the bands observed at 2827, 2838, 2844 cm^{-1} are assigned to CH_2 symmetric stretching vibrations and bands observed at 2909 and 2931 cm^{-1} are assigned to CH_2 asymmetric stretching vibrations. CH_2 symmetric and asymmetric stretching vibrations have been assigned at 2835.8, 2854.6 and at 2910.5 cm^{-1} respectively in FT-laser Raman spectrum, further the scissoring and rocking mode of CH_2 are identified at 1460 cm^{-1} and 729 cm^{-1} respectively. Krishna Kumar and Ramaswamy [31] have also verified these vibrations at 1417 and 756 cm^{-1}.

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